

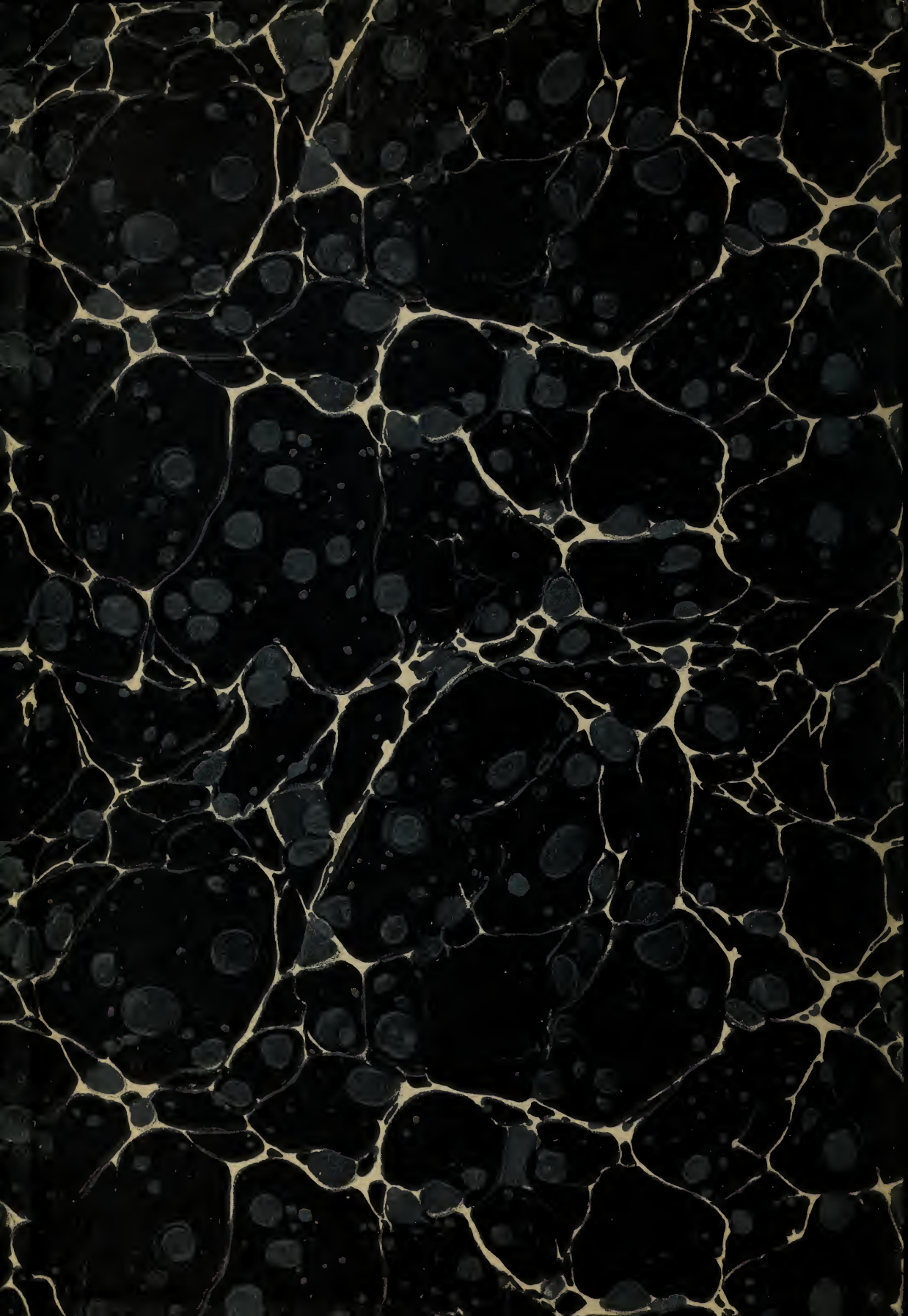
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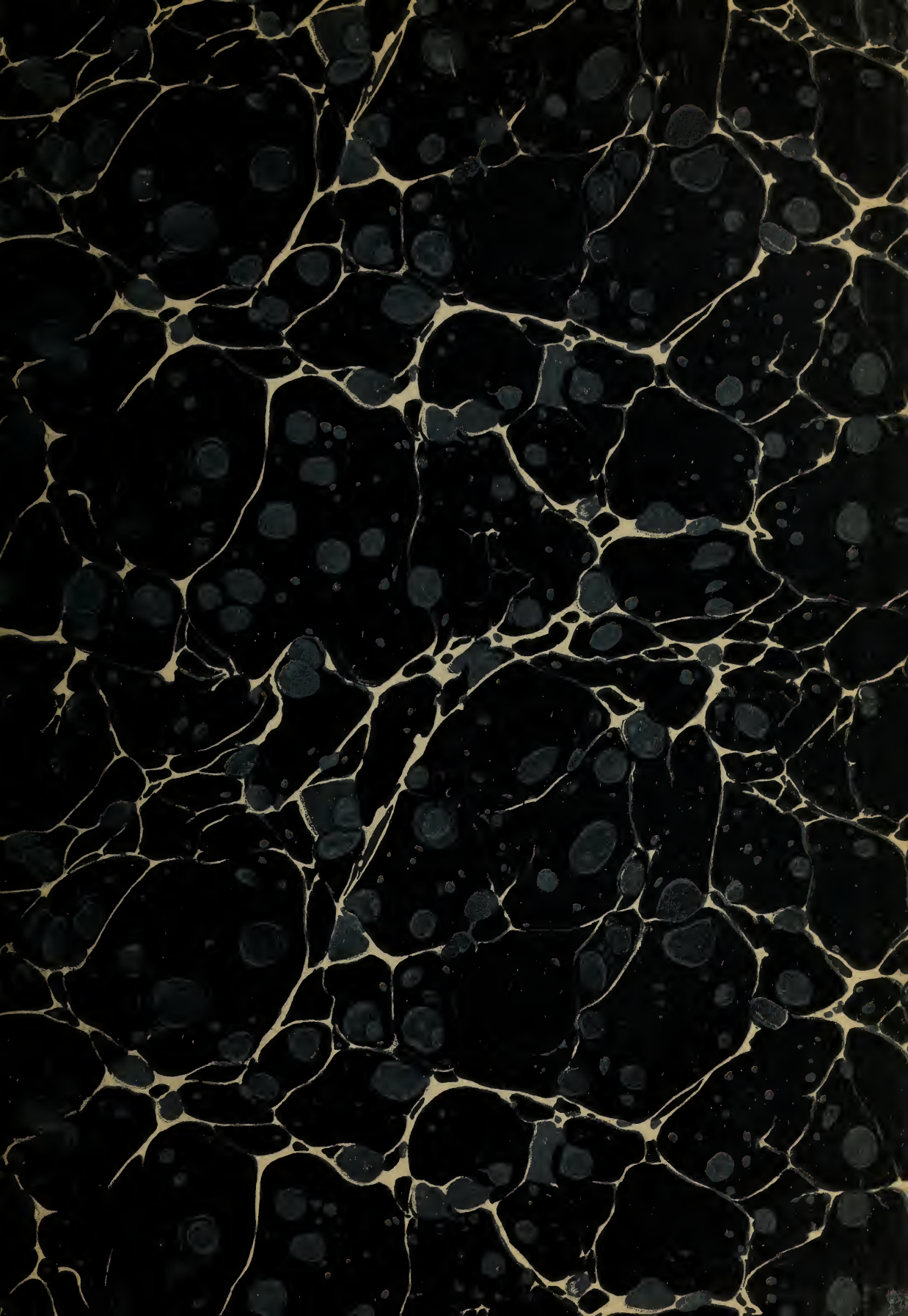
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**TECHNOLOGIC PAPERS**  
OF THE  
**BUREAU OF STANDARDS**

S. W. STRATTON, DIRECTOR

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No. 34

**DETERMINATION OF AMMONIA  
IN ILLUMINATING GAS**

BY

J. D. EDWARDS, Laboratory Assistant

*Bureau of Standards*

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[ MARCH 2, 1914 ]



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# DETERMINATION OF AMMONIA IN ILLUMINATING GAS

By J. D. Edwards

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For "Lacey apparatus" in  
elsewhere read "Hinman  
apparatus."

## I. INTRODUCTION

This paper presents the results of a brief investigation of the apparatus and methods employed for the commercial determination of ammonia in illuminating gas. It forms one of a series of technologic papers of the Bureau which present the results of investigations of methods for testing and analyzing gas. These researches are those on which are based the operating directions given in Bureau of Standards Circular No. 48, "Standard Methods of Gas Testing."

Many refinements of apparatus and manipulation were not incorporated in the work, because it was believed that the accuracy obtainable with the method recommended would be amply sufficient for the purpose for which it was desired, namely, the determination of the presence of ammonia in quantities detrimental to the usefulness of the gas, or sufficient to represent a serious loss of this valuable by-product.

The points which were investigated were the suitability of various indicators, the relative accuracy and convenience of different forms of apparatus, and the various sources of error to which the determination was subject. To have determined the absolute absorptive efficiency of the different forms of apparatus would have necessitated the preparation of a gas containing a known amount of ammonia. It was found impracticable to prepare such a gas, and so the relative efficiency, and from this the probable accuracy, was determined by running the different forms in parallel, using gas from a common supply.

## II. GENERAL CONSIDERATIONS

The method generally used for the determination of ammonia in purified illuminating gas depends upon the absorption of the ammonia in a standard acid solution, the amount of ammonia absorbed from a measured volume of gas being determined either by titration of the acid remaining unneutralized or, less frequently, by allowing the gas to pass until the change in the indicator used shows that all the acid has been neutralized.

The other constituents of the gas which dissolve in the acid affect the actual absorption of the ammonia only as diluents, but in some cases they may seriously interfere with the titration of the unneutralized acid. It is usually assumed that all basic compounds absorbed by the acid are ammonia, the traces of amines present being so small as to be of no importance. There may, however, be present in the gas constituents of an acid character whose presence must be taken into account; the most important of these is carbon dioxide. Hydrogen sulphide, and possibly hydrogen cyanide, may also interfere, but to a less extent, because they are seldom present in more than traces. These gases by



increasing the acidity of the solution might decrease the apparent amount of ammonia found in the gas, but since, in solution, they are all very weak acids the effect of their presence upon the results may be largely eliminated by titrating the excess acid with an indicator not sensitive to them. When the excess acid is titrated outside the apparatus, the interfering gases may be removed by boiling the solution under such conditions as will prevent any loss of acid, but this operation is not desirable if it can be avoided. In any case when the color change is being watched for while the apparatus is in operation, the indicator must show an end point not appreciably affected by the carbon dioxide present.

In gas-inspection work it is frequently only necessary to determine whether the ammonia content of the gas is above or below a certain limit. This can be ascertained by passing through the apparatus an amount of gas sufficient to neutralize the acid used, provided the gas contains the limiting amount of ammonia. If the color of the indicator, previously added to the acid, has then changed, it is known that the limit has been exceeded. In this manner the information desired is obtained without determining the exact quantity of ammonia present. The gas might also be passed through the apparatus until the acid is exactly neutralized, as shown by the indicator; but this, in general, is neither so accurate nor so convenient a method as that of titrating the excess acid, for the end point is hard to determine and the color change must be carefully watched for.

### III. CHOICE OF INDICATORS

The choice of the proper indicator to use for this determination is of greater importance than the choice of apparatus, since the use of an unsuitable indicator may introduce large errors, amounting in extreme cases to more than 100 per cent. Many indicators have been and still are commonly used which are not at all suited to the purpose, failing to meet one or more of the following essential requirements:

1. It should show a sharp end point in dilute solutions.
2. It should be sensitive to ammonia and not be seriously affected by ammonium salts.

3. The end point should be affected as little as possible by carbon dioxide.

An investigation was made of those indicators frequently used for the determination of ammonia in gas and of some others which for theoretical reasons seemed likely to give good results.

#### 1. EFFECT OF CARBON DIOXIDE ON TITRATION

A series of titrations (see Table 1) made under approximately the same conditions that exist in the ammonia determination shows the effect of carbon dioxide on a number of indicators. Titrations of the sulphuric acid were made with sodium hydroxide with each indicator—first, without addition of sodium carbonate; second, after addition of 4 cc of the sodium carbonate solution; and third, after addition of 20 cc of this solution. Although the addition of ammonium sulphate after completing the titration was shown to have no appreciable effect on the end point except when rosolic acid was employed (in which case the addition of 20 cc of the ammonium sulphate solution caused the end point to fade slightly), yet from 2 to 20 cc of the solution was introduced before titration in the cases indicated, to make the conditions more exactly like the conditions during a regular test on the gas. The amount of carbon dioxide probably dissolved from a gas containing 2 per cent of carbon dioxide would be about equal to that introduced by 10 cc of the N/50 sodium carbonate solution. The ammonium sulphate in 2 cc of the solution used was equivalent to that formed by the neutralization of the ammonia from 1 cubic foot of a gas containing 2 grains of ammonia per 100 cubic feet.

The sodium hydroxide solution contained a small amount of carbonate, no attempt being made to prepare a solution entirely free from carbonate. However, comparison of titrations made with and without removal of the carbon dioxide by boiling showed that the amount of carbonate present was negligible as affecting the end point with any indicator of low sensibility toward carbon dioxide.

TABLE 1  
Comparison of Indicators<sup>1</sup>

Indicator.	H <sub>2</sub> SO <sub>4</sub> (cc).	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (cc).	Na <sub>2</sub> CO <sub>3</sub> (cc).	NaOH (cc).	Average.	Apparent equiva- lent of 1 cc Na <sub>2</sub> CO <sub>3</sub> .	Remarks.
Methyl orange	50			44.30			Color change certain at this point; but the point could not be duplicated except by comparison. Color change very gradual.
Sodium alizarin sulphonate	50			44.95			
	50			44.91			
	50	20		44.91	44.92		End point sharp.
	50	2	4	41.14			
	50	2	4	41.17	41.16	0.94	End point good.
	50	10	20	26.30			End point somewhat indefinite.
	50	10	20	26.33	26.32	.93	
Cochineal	50			44.99			
	50			44.96	44.98		
	50	2	4	41.19			Addition of 10 cc (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> after completing titration did not change color of end point appreciably.
	50	2	4	41.21	41.20	.94	End point fair.
	50	10	20	26.41			
	50	10	20	26.43	26.42	.93	End point poor.
Paranitrophenol	50			45.03			
	50			45.16	45.10		Addition of 20 cc (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> after completing titration did not change color of end point appreciably.
	50	2	4	41.42			
	50	2	4	41.41	41.42	.92	End point fair.
	50	10	20	26.88			End point poor. Much more uncertain than with sodium alizarinsulphonate under same conditions.
	50	10	20	27.00	26.94	.91	
Methyl red	50			45.02			End point fair.
	50			45.08	45.05		Addition of 20 cc (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> after completing titration did not change end point appreciably.
	50	2	4	41.49			
	50	2	4	41.40	41.44	.90	End point fair.
	50	10	20	27.10			
	50	10	20	27.10	27.10	.90	End point poor.
Rosolic acid	50			45.96			
	50			45.50	45.88		Addition of 20 cc (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> after completing titration faded end point somewhat.
	50	2	4	42.50			
	50	2	4	42.70	42.60	.82	End point very poor.
	50	10	20	31	31	.74	End point indeterminate; 31 cc is an approximation.

<sup>1</sup> All solutions were approximately N/50 except (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, which was N/25.



The ratio  $\text{H}_2\text{SO}_4 : \text{NaOH}$  as determined with either sodium alizarinsulphonate or methyl red in the absence of carbon dioxide was 1.113. The ratio  $\text{H}_2\text{SO}_4 : \text{Na}_2\text{CO}_3$  under the same conditions was 1.049. From these ratios 1 cc of sodium carbonate is found to be equivalent to 0.94 cc of sodium hydroxide. The column headed "Apparent equivalent of 1 cc of  $\text{Na}_2\text{CO}_3$ " shows the magnitude of the effect of carbon dioxide. The values indicated there are obtained by subtracting the number of cubic centimeters of sodium hydroxide required to neutralize 50 cc of the sulphuric acid in the presence of the indicated amount of sodium carbonate from that required in the absence of the sodium carbonate and dividing this difference by the number of cubic centimeters of sodium carbonate added. The indicators are arranged in the table in the order of their sensibility toward carbon dioxide, methyl orange being the least affected of those tested.

As indicators relatively more sensitive to carbon dioxide are employed, the apparent alkalinity of the sodium carbonate solution decreases. In other words, the carbonic acid formed from the carbon dioxide liberated by the neutralization of the sodium carbonate gives an acid reaction with some of the indicators and must be partially neutralized by the addition of more alkali than is equivalent to the sulphuric acid before the indicator will change color. It will be noted that when using sodium alizarinsulphonate or cochineal the sodium carbonate has practically the theoretical alkali value; that is, equivalent to 0.94 cc of the sodium hydroxide. In the case of paranitrophenol and methyl red this value is slightly less, but still in fair agreement. However, when using rosolic acid the equivalent alkali value is only 0.84 when 4 cc of sodium carbonate is added and indeterminate after the addition of 20 cc.

## 2. CONCLUSIONS AS TO THE CHOICE OF INDICATORS

The indicators which were found to be most suitable for the determination of ammonia in gas were sodium alizarinsulphonate, cochineal, and paranitrophenol. The applicability of these, as well as other common indicators, is pointed out in the following paragraphs:



*Sodium alizarinsulphonate* was found to be excellently adapted for the determination of ammonia, giving uniformly good results. Its first color change is from greenish yellow to brown, and is quite sharp, even with very dilute solutions. There is a further change to rose red, but the first one should be taken as the end point. A 1 per cent aqueous solution of sodium alizarinsulphonate should be used. Two drops of the indicator solution in a volume of 100 to 150 cc will be found sufficient with this, as well as the other indicator solutions given. The end point is not affected by the ammonium salts present, and the effect of the carbon dioxide in the solution is negligible.

*Cochineal* changes from brownish rose to lilac. The color change is not as sharp as with sodium alizarinsulphonate, but it will give good results if properly prepared and used. The indicator solution may be prepared by grinding in a mortar 3 g of cochineal with 250 cc of 25 per cent alcohol in the cold and filtering off the undissolved residue.

*Paranitrophenol* gives a sharp color change, from colorless to yellow, which can be easily recognized. It is more sensitive to carbon dioxide than the first two indicators mentioned, but the results are not seriously affected unless the gas is high in carbon dioxide. A solution of 2 g in 100 cc of 25 per cent alcohol may be used.

The following indicators are either useless or unsatisfactory for the several reasons given:

*Methyl orange* is less sensitive to carbon dioxide than any of the above indicators, but its color changes are very gradual and the fixing of the end point is difficult, particularly with weak solutions.

*Phenolphthalein* can not be used because it gives an acid reaction with even small amounts of carbon dioxide in solution, and because results with it are inaccurate in the presence of ammonium salts.

*Litmus* can not be used, both because its end point is affected by carbon dioxide and because its color changes are too gradual and indistinct to fix the end point with the requisite degree of certainty.

*Congo red* is not satisfactory because its end point is not sharp enough.

*Rosolic acid* is too sensitive to carbon dioxide.

*Methyl red* has about the same degree of sensibility toward carbon dioxide as paranitrophenol, but the color change from pink to pale yellow is too indefinite.

*Hematoxylin* is not satisfactory because its color changes are variable and transitory. The indicator solution is not stable in the air.

#### IV. EFFECTS OF GLASS BEADS

The presence of the glass beads which are used in some of the absorption apparatus may lead to erroneous results for two reasons: First, the beads may yield alkali on contact with the absorbing liquid, and, second, washing of the beads may be incomplete.

##### 1. ERRORS DUE TO SOLUBILITY OF BEADS

The amount of alkali dissolved from the beads depends upon the kind of glass from which they are made, the surface exposed, and the time they are exposed to the absorbing liquid. Although the absolute amount of alkali thus introduced is small, it may be equivalent to a considerable percentage of the total amount of ammonia to be absorbed.

The solubility of the beads can only be determined by experiment, and each operator should test the beads intended for use in the absorbing apparatus. The test may be conducted in the following manner: Wash 100 or 150 cc of the beads thoroughly with distilled water and dry them completely. Place the beads in a dry flask and add 100 cc of the acid to be used in the regular determination. Prepare a blank by placing 100 cc of the same acid in a similar flask. Stopper both flasks tightly and let stand for some convenient period, say 12 or 24 hours. Then, after thoroughly mixing, pipette out 25 cc portions from each and titrate with standard alkali. After a further interval titrate another 25 cc portion. The probable loss of acid from the beads during a determination lasting one or two hours can then be calculated. The permissible loss from this source must be determined by the operator, giving due consideration to the amount of ammonia being determined and the degree of accuracy required.

Tested in this manner the beads used in the Referees apparatus, which were of perforated cut glass 8 to 10 mm in diameter, neutralized 2 per cent of the acid in 24 hours, there being a further loss of only 0.2 per cent in the next 5 hours.

The beads used in the Emmerling, which were perforated glass beads of the usual shape, 4 to 6 mm in diameter, neutralized 1.5 per cent of the acid in 24 hours, there being no further determinable loss after 5 hours more.

A third sample, of solid spherical beads 2 to 5 mm in diameter, was also tested. These neutralized from 40 to 60 per cent of the acid in 24 hours, and there was a further considerable neutralization during the next 5 hours. Since continued soaking did not appreciably reduce their solubility, these beads were evidently unsuitable and were not used in any of the remaining experimental work.

## 2. ERRORS DUE TO INCOMPLETE WASHING

The washing of a large column of beads to render them free from acid is an operation which is tedious and uncertain, particularly when the volume of wash water which it is permissible to use is comparatively small. The difficulties of titrating a small amount of acid increase greatly with dilution of the acid, and so it is quite necessary that the amount of wash water should be kept as low as possible. Perforated beads especially retain traces of the acid very tenaciously and about the only certain method of removing the last traces of acid is to completely cover the beads with several portions of the wash water; merely allowing the water to run over the beads is not sufficient. In the Referees apparatus, however, the chamber occupied by the beads is quite large, and it is impracticable to fill the apparatus completely with water when washing it out. The best plan, therefore, is to use several 50 to 75 cc portions of water and allow each portion to wash the beads as much as possible by rotating the cylinder before draining.

The bead column in the Emmerling tower required only 30 cc of wash water to flood the beads, and washing could be made practically complete with less than 100 cc of water.



TABLE 2

Loss of Acid in Washing Out Apparatus Containing Beads<sup>2</sup>

Apparatus.	H <sub>2</sub> SO <sub>4</sub> added (cc N/50).	H <sub>2</sub> SO <sub>4</sub> unrecovered (cc N/50).	NH <sub>3</sub> equivalent of H <sub>2</sub> SO <sub>4</sub> lost (grains per 100 cu. ft. calcu- lated for 1 cu. ft. sample).
Referees apparatus.....	28.83	0.22	0.11
	28.45	.08	.04
	15.00	.27	.14
	15.06	.20	.10
Emmerling tower.....	15.47	.07	.04
	15.02	.03	.02

<sup>2</sup> Sodium alizarinsulphonate used as indicator. Three 75 cc portions of wash water used in Referees; two 30-cc portions used in Emmerling.

Table 2 shows the losses which occurred in several experiments in washing out both the Referees apparatus and the Emmerling tower. The acid was placed in the apparatus, allowed to come in contact with all the beads, and then washed out just as in the regular determination. The time in the apparatus was less than 10 minutes, so that the results are not affected by the solubility of the beads. The last portion of wash water used gave a neutral reaction with the indicator. It will be observed that practically all of the acid is recovered from the Emmerling tower; but the losses in the Referees apparatus are somewhat variable, being appreciable, but nevertheless small enough to be negligible in any ordinary work.

To insure completeness of washing, the operator should test his procedure by placing in the apparatus the amount of acid used in a determination and washing with successive portions of wash water until a portion is secured which is neutral to the indicator used. If the amount of wash water thus shown to be necessary is excessive, the volume of each portion should be reduced and the number increased as may be necessary.



## V. TESTS OF APPARATUS

## 1. DESCRIPTION OF APPARATUS

Various forms of gas wash bottles have been used for absorbing the ammonia, but a few special types have best met the conditions of service and come into practical use. The following five forms have been considered in this paper.

(a) **Referees Apparatus.**—The Referees apparatus is the well-known form, first used by the London Gas Referees. It consists of a glass cylinder filled with beads and having stopcocks at one or both ends. Some dealers are supplying this apparatus with metal cocks or connections cemented to the glass ends; but both the cement and the metal are quickly attacked by the acid and make results obtained by the use of such apparatus unreliable. The form figured is that used in these tests. It was necessary to have

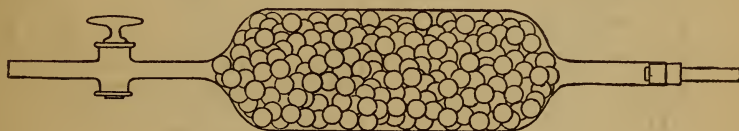


Fig. 1.—Referees apparatus ( $\frac{1}{4}$  size)

a stopcock at one end so that the apparatus could conveniently be held vertically when filling with acid, but the tube at the other end, which was used as the outlet, was made without stopcock and larger, so that acid and wash water could be easily introduced. In this outlet was placed a perforated rubber stopper carrying a glass tube.

(b) **Emmerling Tower.**—Although the Emmerling tower is also filled with beads, it is essentially different from the Referees form in operation, for the gas is required to bubble through the acid, while in the Referees apparatus it only passes over the surface of the acid. Emmerling towers are made in many different sizes and proportions, the one used (Fig. 2) being of 2.2 cm internal diameter and holding conveniently a bead column 10 cm in length, which was found to give satisfactory results. The usual form is illustrated, but it could be better adapted for this particular purpose by plac-

ing the outlet tube on the same side as the inlet, or by using a glass tube in the rubber stopper as the outlet. Then there would be no danger of losing acid through the outlet if the apparatus was inclined too near to the horizontal.

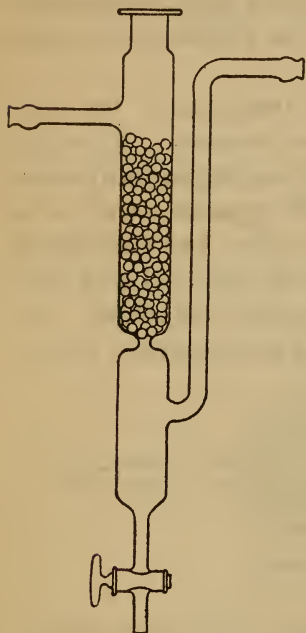


Fig. 2.—Emmerling tower  
( $\frac{1}{4}$  size)



Fig. 3.—Lacey apparatus ( $\frac{1}{4}$  size)

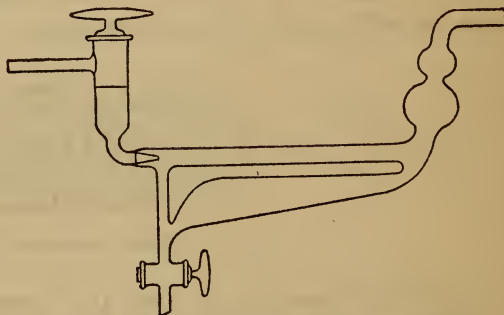


Fig. 4.—Modified Cumming wash bottle ( $\frac{1}{4}$  size)

(c) **Lacey Apparatus.**—This apparatus was primarily designed for traveling inspection work, and being small and light it is readily portable. The form and construction of the Lacey is apparent from Fig. 3.

(d) **Modification of Cumming Wash Bottle.**<sup>3</sup>—This apparatus was designed at the Bureau of Standards for this work. (See Fig. 4.) The object in view was to obtain a gas wash bottle which would operate under low pressure and yet give complete absorption and

<sup>3</sup> Chem. News, 101, 39; 1910.

continuous circulation of the acid. Furthermore, it was so constructed that it may be permanently connected, as when used in series with the sulphur apparatus, and be filled and washed out without changing any of the connections. The gas passing through the small nozzle acts like an injector and circulates the liquid rapidly and continuously, thus bringing fresh acid into contact with the gas. Any color change of the indicator can therefore be easily determined, for the liquid is very nearly of constant composition throughout the apparatus.

(e) **Wash Bottle.**—The common gas wash bottle was tested because its availability is a strong point in its favor when it is to be used in gas-inspection work where the other forms might not

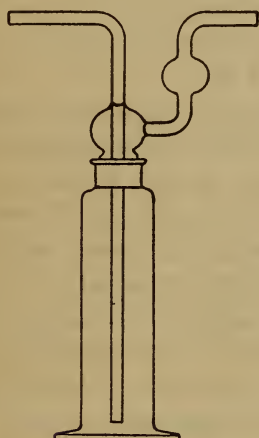


Fig. 5.—Wash bottle ( $\frac{1}{4}$  size)

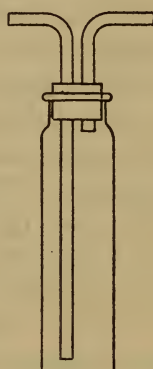


Fig. 6.—Wash bottle ( $\frac{1}{4}$  size)

be obtainable. The form used (Fig. 5) was of glass with a ground glass joint at the top, but one just as efficient can be easily made from a tall glass bottle, closed with a rubber stopper bearing an inlet and an outlet tube as shown in Fig. 6. The depth of liquid in the bottle as well as the size and shape of the bottle will affect the absorption, but the depth of liquid is limited by the gas pressure available for its operation. In the following experiments the bottle used had an internal diameter of 4 cm, was 18 cm high, and the gas bubbled through 4 to 6 cm of solution.



## 2. COMPARISON OF APPARATUS

(a) **Meter Comparison.**—For comparison, four different forms of apparatus were run at the same time from a common gas supply under as nearly uniform conditions as possible. The gas meters employed were all of the wet type. Since only comparative results were desired, the meters were not calibrated, but compared with one another by running them in series. This comparison was repeated at intervals throughout the work and the agreement found to be satisfactory, no change taking place large enough to have any appreciable effect upon the results. When only 1 or 2 cubic feet are used in a determination, the error incident to taking fractional parts of a revolution of the meter may be appreciable; it might amount to 1 per cent of the volume of the gas if only 0.5 cubic foot is used. The effect of this error would, of course, be reduced by using a larger amount of gas.

(b) **Gas Supply.**—The regular city gas supplied to the Bureau was used, but in a large number of the runs ammonia was added to it, since its normal content is only about 1 grain per 100 cubic feet.<sup>4</sup> The ammonia was introduced into the gas by means of the following apparatus: A 30-liter bottle was fitted with a rubber stopper bearing two inlets and a stirring apparatus. This latter, consisting of a small fan inserted through the stopper and operated by a small electric motor, served to mix thoroughly the contents of the bottle. The gas was introduced through one inlet and a smaller amount of gas, which had passed through a tube containing several lumps of ammonium carbonate, through the other. This latter gas bubbled through a small wash bottle before passing through the ammonium carbonate tube, so that the amount of ammonia being introduced could be gauged approximately by the number of bubbles of gas passing per minute. The gas, after being mixed in the first bottle, passed through an outlet near the bottom into a similar bottle through a narrow glass tube reaching two-thirds of the way to the bottom. The gas

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<sup>4</sup> Although it is the universal practice in this country to express the results in grains ammonia per 100 cubic feet of gas, these figures convey no adequate impression of the volume relation of the ammonia to the other constituents of the gas. One grain of ammonia per 100 cubic feet, measured at 30 inches and 60° F (762 mm and 15.55° C), is equivalent to 31.6 parts of ammonia per million by volume.



used was withdrawn from the top of this second bottle and distributed through a system of T-connectors, delivering the same quality of gas to each apparatus. All connections were made as far as possible by means of glass tubing held together by short pieces of heavy walled rubber tubing.

(c) **Absorbing Liquid.**—An approximately N/50 solution of sulphuric acid, standardized by precipitation with barium chloride, was used as the absorbing agent.

For titrating the excess acid a solution of sodium hydroxide of approximately equivalent strength was used, the exact ratio between it and the acid being obtained by titration in the same volume of solution as during an actual determination.

It was not considered desirable to use a stronger solution of acid because of the small amount of ammonia to be absorbed and the fact that small errors in the measurement of stronger solutions make a large error in the ammonia apparently absorbed. Should it be desirable to extend the operation over long periods of from 10 to 20 hours, in order to obtain an average for that period, it may be necessary to use a stronger acid solution. The amount of ammonia likely to be absorbed is the factor which should determine the strength of acid to be used. Other conditions being equal, the greatest accuracy is obtained when the major part of the acid in the apparatus is neutralized by the ammonia in the gas.

(d) **Operation of Apparatus.**—About 25 cc of the standard acid was placed in each of the different forms of apparatus, except the Lacey, which required only about 15 cc; then a small amount of water was added, to bring the solution in each up to the volume required for its most efficient operation. Connection was then made between the gas mixing bottle and the apparatus, and a meter was connected to the outlet of each apparatus. All four forms were started at the same time and the flow of gas to each was carefully adjusted to the desired rate. Although the rate fluctuated somewhat, owing to changes in the gas pressure, no governor being used, it was maintained as nearly uniform as possible by close observation and regulation. The rate given in the table is the average rate for the whole run.

TABLE 3  
Comparison of Ammonia Absorption Apparatus <sup>5</sup>

Test num- ber.	Time of run, min.	Average NH <sub>3</sub> , grains per 100 cu. ft.	Lacey.		Modified Cumming.				Wash bottle.				Referees.			Emmerling.			
			Rate, cu. ft. per hr.	NH <sub>3</sub> , grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH <sub>3</sub> , grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH <sub>3</sub> , grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH <sub>3</sub> , grains per 100 cu. ft.	Variation from average, per cent.	Rate, cu. ft. per hr.	NH <sub>3</sub> , grains per 100 cu. ft.	Variation from average, per cent.		
1	60	20.50	0.5	19.48	-5.0	0.5	20.91	+2.0					0.5	20.36	-0.7	0.5	21.24	+3.6	
2	85	12.25	.54	12.42	+1.4	.56	12.34	+0.7					.50	11.98	-2.2	.54	12.26	0.0	
3	70	11.68	.6	11.81	+1.1	.6	11.74	+0.5		0.63	11.52	-1.4				.65	11.65	-0.3	
4	100	6.81	.65	6.78	-0.4	5	6.74	-1.0					.5	6.82	+0.1	.5	6.90	+1.3	
5	90	6.42	.61	6.46	+0.6	62	6.44	+0.3		.57	6.31	-1.7				.60	6.46	+0.6	
6	120	5.33	.78	5.45	+2.2	.57	5.26	-1.3		.64	5.23	-1.9				.68	5.38	+0.9	
7	120	3.85	.77	3.77	-2.1	.66	3.77	-2.1		.72	3.72	-3.4				.73	4.13	+7.3	
8	120	3.66	.53	3.67	+0.3	.53	3.55	-3.0					.56	3.77	+3.0	.51	3.66	0.0	
9	60	2.69	.60	2.79	+3.7	.60	2.72	+1.1		.61	2.60	-3.3				.60	2.65	-1.5	
10	270	.80	.63	.79	-1.3	.62	.80	0.0		.59	.77	-3.8				.64	.83	+3.8	
11	60	6.38	1.10	6.34	-0.6					.98	6.38	0.0		1.03	6.40	+0.3	1.05	6.38	0.0
12	60	3.99	1.00	3.90	-2.3					.98	3.90	-2.2		1.01	4.14	+3.8	.97	4.00	+0.2
13	105	.95	1.00	.92	-3.1									1.01	1.01	+6.3	1.01	.93	-2.1
Average, 1 to 10.					+0.5			-0.3				-2.6							+1.6
																			+0.05

<sup>5</sup>Sodium alizarinsulphonate used as indicator.

(e) **Results of Comparison.**—Table 3 shows the results of 13 runs with gas of varying ammonia content. The data for each run are arranged in a single line, designated at the left by the number of the test. All results secured are recorded with the exception of two runs where irregularities of operation interfered and made the results valueless, despite the fact that fair agreement was secured. The value recorded in column three, "Average  $\text{NH}_3$ , grains per 100 cu. ft.," is obtained by averaging the four results obtained with the different apparatus. The values in the column headed "Variation from average" are the differences between the average and the value secured with that particular apparatus expressed as a percentage of the average. While the average value may be no nearer the correct value than any of the four individual results, it affords a convenient means of comparison and the results indicate the general tendency of the different forms of apparatus. The average variation from the mean as shown at the foot of the table is only for tests 1 to 10, since the last three were made at a much higher rate and, therefore, are not comparable on the same basis as the others. Two different Referees apparatus were used, identical in shape, but one slightly smaller than the other. Tests 4, 11, 12, and 13 were made with the smaller apparatus. Sodium alizarinsulphonate was used as the indicator, and the excess acid titrated in every case except with the Lacey apparatus in tests 1 and 2, where gas was passed through the apparatus until the change of color of the indicator indicated saturation of the acid by the ammonia.

It is seen from a consideration of these results that those obtained with the Emmerling tower are somewhat higher than those obtained with the other forms, and that the wash bottle gives results consistently lower. The other three ran about the same.

In order to determine whether any appreciable amounts of ammonia escaped unabsorbed, a second series of tests (Table 4) was made. In these tests the gas after leaving the first absorption apparatus passed through an Emmerling tower, the acid in which was then titrated as usual. Since the gas receives a very thorough washing in its passage through this apparatus, it is reasonably certain that any ammonia escaping absorption in the Emmerling



tower thus used must be a very small percentage of the total and in any case entirely without interest as affecting the quality of the gas. As seen in Table 4, in all but two of the experiments the amount of ammonia thus absorbed in the Emmerling tower was not detectable within the limits of error of the titration.

TABLE 4  
Tests of Completeness of Absorption <sup>6</sup>

First absorption apparatus in series with Emmerling.	Rate of passage of gas, cu. ft. per hour.	NH <sub>3</sub> , grains per 100 cu. ft.	NH <sub>3</sub> in Emmerling, grains per 100 cu. ft.	Percentage of NH <sub>3</sub> absorbed in second bottle.
Lacey.....	0.62	9.64	0.0	0
	.66	21.65	.2	1
Referees.....	.60	25.60	.0	0
	.66	8.50	.0	0
Modified Cumming.....	.52	15.20	.0	0
	.57	5.34	.0	0
Wash bottle.....	.61	4.26	.0	0
	.57	4.53	.1	2

<sup>6</sup> Titrations made with sodium alizarinsulphonate as indicator.

### 3. CONCLUSIONS AND RECOMMENDATIONS REGARDING APPARATUS

The accuracy obtained in practice will, of course, depend upon the accuracy with which the gas is measured, the certainty with which the ammonia equivalent of the acid is known, and the completeness of absorption of the ammonia. With careful operation, any one of the five forms of apparatus tested would ordinarily give results that are well within the limits of accuracy required for this determination, either for commercial control work or for the purpose of gas inspection.<sup>7</sup> The wash bottle appears to be slightly less efficient as an absorber than the other forms, but still it gives satisfactory results. Any increase in the accuracy which might be secured by a more complete absorption train and the removal of interfering gases would not generally be practicable because of the increase in time and labor involved.

<sup>7</sup> It is difficult to make any comprehensive statement defining satisfactory results. In general, results on gas containing up to about 5 grains of ammonia per 100 cubic feet should be within 10 per cent of the ammonia content of the gas, although the percentage error may be greater when the ammonia is 1 grain or lower. With gas containing more than 5 grains ammonia, the percentage error should decrease somewhat. The interpretation of results is discussed in Bureau of Standards Circular No. 43.

*Referees apparatus.*—Balancing the possible loss of acid due to neutralization by alkali from the beads or by retention of acid after washing is the possibility of ammonia escaping from the Referees apparatus; a danger somewhat greater than with other forms because the gas passes over only the wet surface of beads and cylinder and may quickly saturate the acid exposed without neutralizing the main bulk of liquid in the bottom of the apparatus. It was frequently observed, when an indicator had been added to the acid, that the beads along the top had changed color because of saturation by the ammonia of the liquid adhering to them and that this color change sometimes extended to the outlet, the bulk of the liquid being still unaffected. Owing to the solubility of the ammonia in water there may be no loss even after the surface liquid has become saturated, but it is believed that ammonia sometimes escapes this way. The cylinder should be rotated from time to time to moisten the top beads with fresh acid. The cylinder should also be completely filled with beads, so that there is small opportunity for the gas to follow channels and so escape thorough washing. At higher rates, up to 1 cubic foot, the Referees apparatus gives better absorption than either the Lacey or the modified Cumming. The Referees apparatus, as noted in a previous paragraph, should be made without metal parts, and the outlet is best closed with a rubber stopper carrying a glass tube. As this apparatus is clumsy to handle it is not recommended for traveling work. However, it operates with very small difference of pressure between inlet and outlet, which is frequently a great advantage, particularly when being used in series with a sulphur apparatus.

*Emmerling tower.*—The Emmerling tower seems to give somewhat better absorption than the other forms. Since only a small column of beads is used, it can be easily washed by bubbling a little air through to agitate the wash water covering the beads. The same attention should be paid to the resistance to solution of the beads used as with the Referees apparatus. The principal objection to the Emmerling form is the fact that it requires a larger pressure to operate than some of the other forms. The pressure necessary depends, of course, on the amount of liquid in the appa-

ratus and the angle at which it is inclined. In addition to its efficiency as an absorber, another point in its favor is the fact that it can be filled and emptied without breaking the connections. It may be used at higher rates, say 1 cubic foot per hour, with safety.

*Lacey apparatus.*—The Lacey is a satisfactory form to use; it is light and easily portable, being especially adapted for traveling inspection work. The circulation of acid is often poor, and when a test is being run to determine whether saturation of the acid has taken place it is necessary to mix the contents of the bulbs thoroughly before a reliable observation can be made. The Lacey should be so filled and set that the gas is required to bubble past each of the constrictions. Care should be taken that loss of acid does not occur by bubbles breaking too close to the outlet. The gas should be passed at about 0.6 cubic foot per hour.

*Modified Cumming apparatus.*—This apparatus gives good absorption when run at rate of 0.6 cubic foot per hour or less. The circulation of the liquid is excellent and any change of color can be easily observed. The pressure required to operate it is low. It can be permanently connected, being emptied and filled without changing the connections, which makes it very convenient to use in a permanent set up in series with a sulphur apparatus.

*Wash bottle.*—The wash bottle is evidently not quite as efficient an absorber as the other forms. Where an accuracy of 10 per cent is sufficient the wash bottle may be found useful because of its availability. The bottle should be tall and narrow, the amount of acid being used depending on the pressure available for its operation. Two bottles in series may be used where greater accuracy is desired. They will require greater pressure to operate, which may prevent their use where the pressure is low. Gas should be passed at a rate not greater than 0.5 to 0.6 cubic foot per hour.

## VI. SUMMARY AND RECOMMENDATIONS

Four common forms of apparatus for the determination of ammonia in gas, and a new form designed on the principle of the Cumming wash bottle were tested. The results show that the amount of ammonia in a gas can be determined with sufficient



accuracy for official or commercial testing with any of the five forms. The advantages and disadvantages of each form as well as precautions to be observed in operation are pointed out in the text.

It is recommended that the ammonia be determined by absorption in sulphuric acid with subsequent titration of the excess acid and not by passing gas through the apparatus until a color change is shown by the indicator. It is satisfactory, however, when it is only desired to know whether the ammonia content is above or below a certain limit, to pass a predetermined volume of gas and note whether the acid has been completely neutralized or not.

Sodium alizarinsulphonate, cochineal, and paranitrophenol have been found to be satisfactory indicators.

The use of a N/50 solution of sulphuric acid as an absorbing agent is recommended, although the strength may be varied to meet different conditions.

The errors due to incomplete washing and the use of glass beads are discussed, and means of eliminating their effect are given.

Full directions for carrying out the determination, preparation of standard solutions, calibration and use of meters, etc., will be found in Bureau of Standards Circular No. 48, "Standard methods of gas testing."

To Mr. R. S. McBride are due the author's thanks for the continued help and advice given during the course of this work. Preliminary experiments on this determination were made by Mr. E. R. Weaver, and the author wishes to express also his appreciation of the assistance gained from Mr. Weaver and his experience.

WASHINGTON, March 2, 1914.



## APPENDIX

The following is a list of the names of the persons who have been named in the text of the book, and who have been named in the text of the book, and who have been named in the text of the book.

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